

# Thermal aging of hydrogenated nitrile rubber – loss of additives and its influence on elasticity maintenance<sup>\*)</sup>

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**Abstract:** The thermal aging of hydrogenated nitrile rubber (HNBR) at elevated temperatures 125 and 150 °C was investigated. The changes of chemical structures, including functional groups and crosslinking density, and the changes of mechanical properties, including recovery from bending (*RFB*), tensile strength, elongation at break and Young's modulus, were determined. In addition, the loss of additives was analyzed by pyrolysis gas chromatography-mass spectrometry (Py-GC/MS). The aging procedure of HNBR exhibited two stages: loss of additives along with the deterioration of elasticity; obvious oxidation and extra crosslinking with further hardening and embrittlement. The relationship between the deterioration of elasticity and the loss of plasticizers was established. It was demonstrated that the failure of HNBR happened long before obvious oxidation and crosslinking of the rubber chains, and the loss of additives, especially the loss of plasticizers, was the main reason for the failure. Therefore, the elasticity recovery of aged HNBR immersed in the plasticizer (*n*-propyl palmitate as a model) was carried out. This treatment was demonstrated to be effective before obvious oxidation and crosslinking of HNBR occurred during the thermal aging.

**Keywords:** hydrogenated nitrile rubber, thermal aging, additives, elasticity.

## Starzenie termiczne uwodornionego kauczuku nitrylowego – ubytek dodatków i jego wpływ na zachowanie elastyczności

**Streszczenie:** Badano starzenie termiczne uwodornionego kauczuku nitrylowego (HNBR) w temperaturze 125 i 150 °C. Określono zmiany struktur chemicznych, w tym grup funkcyjnych i gęstości usieciowania oraz zmiany właściwości mechanicznych, w tym powrotu poodkształceniowego po zginaniu (*RFB*), wytrzymałości na rozciąganie, wydłużenia przy zerwaniu i modułu Younga. Ponadto metodą pirolitycznej chromatografii gazowej z detekcją mas (Py-GC/MS) analizowano straty dodatków obecnych w kauczuku. Procedura starzenia się HNBR wykazywała dwa etapy: ubytek dodatków wraz z pogorszeniem elastyczności; wyraźne utlenianie i dodatkowe sieciowanie związane z dalszym utwardzaniem i zwiększaniem kruchości. Określono zależność pomiędzy zmniejszaniem się elastyczności a ubytkiem dodatków zmiękczających. Wykazano, że pogorszenie właściwości HNBR następowało znacznie wcześniej niż utlenianie i sieciowanie oraz było spowodowane utratą dodatków, a zwłaszcza plastyfikatorów. W związku z tym przeprowadzono próbę odtworzenia elastyczności starzonych próbek HNBR przez zanurzenie w plastyfikatorze (palmitinian *n*-propylu jako model). Obróbka ta okazała się skuteczna, pod warunkiem przeprowadzenia jej zanim podczas starzenia termicznego nastąpiło utlenianie i sieciowanie HNBR.

**Słowa kluczowe:** uwodorniony kauczuk nitrylowy, starzenie termiczne, dodatki, elastyczność.

Hydrogenated nitrile rubber (HNBR) is prepared by selective hydrogenation of the carbon-carbon double bonds in nitrile rubber (NBR) [1]. Since Bayer and Zeon Company developed this new kind of elastomer in 1980s, HNBR has attracted great interests in investigation and

utilization [2]. HNBR not only exhibits excellent oil and chemical resistance (like NBR), but also is well known for its good balance among low-temperature flexibility, high static and dynamic mechanical strength, abrasion resistance, and good heat resistance [3]. Therefore, HNBR

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is widely used in automotive, industrial and other applications where high heat and oil resistance are required, such as automotive engine bay, sealing and piping equipment [4, 5].

Research on HNBR mainly focused on the mechanical property improvement by adding fillers [6–12] or blending with other elastomers [13–17]. For example, zirconium tungstate was added to control the thermal expansivity of HNBR and increase its modulus [18]. Blending HNBR with fluorocarbon rubber (FKM) improved the thermal resistance of HNBR, as well as the low-temperature resistance of FKM [19].

In addition, aging property of HNBR was affected by adding nanofillers like carbon nanotubes and organo-modified clay, or by blending with other elastomers like ethylene-vinyl acetate rubber [20–24], as well as by adjusting the processing parameter, the acrylonitrile content and the level of unsaturation of the rubber [25, 26]. There were several papers referred to the chemical structure changes of HNBR during aging. Infrared spectroscopy studies showed that the generation of C=O and COOR groups, and the increase of the apparent crosslink density dominated the aging process [27, 28]. Recently, the scratch behavior of aged HNBR, aging of real seals and aging of HNBR in sour gas came into view [29–31]. However, the loss of additives and its relationship with the deterioration of mechanical properties of HNBR have not been reported yet.

According to our prior study on thermal aging of NBR, the loss of additives is crucial for the deterioration of mechanical properties of NBR [32–36]. The aim of this study was investigation of physical and chemical changes of HNBR, as well as the loss of additives during the thermal aging.

## EXPERIMENTAL PART

### Materials

Vulcanized hydrogenated nitrile rubber (HNBR) sheets with thickness of 2 mm were supplied by SKF/Engineering and Research Center (Netherlands). The acrylonitrile (ACN) content in the rubber was 36 wt % and the degree of saturation was 96 %. Thermal aging was carried out in air-circulating oven at 125 and 150 °C for up to 1000 h.

### Methods of testing

#### ATR-FTIR

Infrared spectra were obtained using a Thermo-Nicolet 6700 FTIR spectrometer equipped with an attenuated total reflection accessory (ATR-FTIR) by signal averaging 32 scans at the resolution of 4 cm<sup>-1</sup> in the wavenumber range of 650–4000 cm<sup>-1</sup>. Three parallel measurements were carried out for each test.

### Solvent swelling test

Crosslinking densities of the samples before and after aging were measured by solvent swelling test. Samples of 0.1–0.2 g were weighed and then soaked in butanone for 96 h. The swollen samples were weighed and then dried at 105 °C in an air-circulating oven for at least 4 h. The weights of dried samples were measured. The volume swelling rate (*VR*) of each sample, representing the crosslinking density, was calculated by the following equation:

$$VR = \frac{\frac{m_i \cdot P_M}{d_M}}{\frac{m_i \cdot P_M}{d_M} + \frac{m_s - m_d}{d_s}} \quad (1)$$

where:  $m_i$  – the mass of the initial sample,  $m_s$  – the mass of the swollen sample,  $m_d$  – the mass of the dried sample,  $P_M$  – the mass fraction of the matrix in the rubber, 0.439,  $d_M = 0.98$  g/cm<sup>3</sup> – the density of the matrix,  $d_s = 0.8054$  g/cm<sup>3</sup> – the density of the solvent (butanone).

Two parallel measurements were carried out for each test.

### Recovery from bending

Recovery from bending (*RFB*) test was carried out following the standard ASTM D6515. Test specimens with the size of 100 × 10 mm were cut from the original sheets. Three parallel measurements were carried out for each test.

### Recovery of *RFB*

The *RFB* specimens of HNBR aged at 150 °C for 72 h in an air-circulating oven were taken out and immersed into IRM903 oil, *n*-propyl palmitate, or just stored at ambient condition (in air). After several days, specimens were taken out, and their *RFB* values were measured, following the procedures 8.5.3 to 9.1 in ASTM D6515.

For comparison, vulcanized nitrile rubber (NBR) sheets with thickness of 2 mm supplied by Institute of Aeronautical Materials, China, were also tested. The *RFB* specimens of NBR were aged at 125 °C for 288 h in an air-circulating oven, then the specimens were taken out and immersed into IRM903 oil, *n*-propyl palmitate, or just stored at ambient condition and after several days their *RFB* values were measured according to the same standard.

### Tensile test

Tensile tests were carried out following the standard ASTM D412. The dumbbell-shape samples were cut from the original sheets. Three parallel measurements were carried out for each test.

### Py-GC/MS

An EGA/PY-3030D multi-shot pyrolyzer (Frontier Laboratories Ltd., Japan) was equipped on a gas chromatography-mass spectrometry (GCMS-QP2010 SE, Shimadzu, Japan). The flash evaporation technique was used to separate volatile components from HNBR by heating samples (1.0 mg) at 350 °C for 0.5 min. Samples were cut to various depths from the surface of a HNBR sheet, *i.e.*, 0, 0.25 or 0.5 mm. The thickness of each sample was approximately 0.2 mm. The volatiles were carried by helium through a melted silica capillary column (Ultra alloy-5, 30.0 m, i.d. 0.25 mm x 0.25  $\mu$ m stationary phase thickness) and the mixture was separated for identification. The oven temperature was held at 50 °C for 1 min, then raised at a rate of 8 °C/min to 300 °C, and held for 30 min.

Finally, each component was identified by MS detector with EI source and mass range of  $m/z$  33–600. The MS spectrum was compared to standards in NIST 11 database composed of *ca.* 240 000 standard spectra.

### RESULTS AND DISCUSSION

#### Change of chemical structures and mechanical properties during thermal aging

Changes of chemical structures and mechanical properties during thermal aging of HNBR were investigated. The changes of relative peak intensities of hydroxyl (O-H, 3641–2987  $\text{cm}^{-1}$ ), alkyl (C-H, 2920  $\text{cm}^{-1}$  and 2851  $\text{cm}^{-1}$ ) and carbonyl (C=O, 1716  $\text{cm}^{-1}$ ) groups of HNBR at different temperatures are shown in Fig. 1. The values were de-

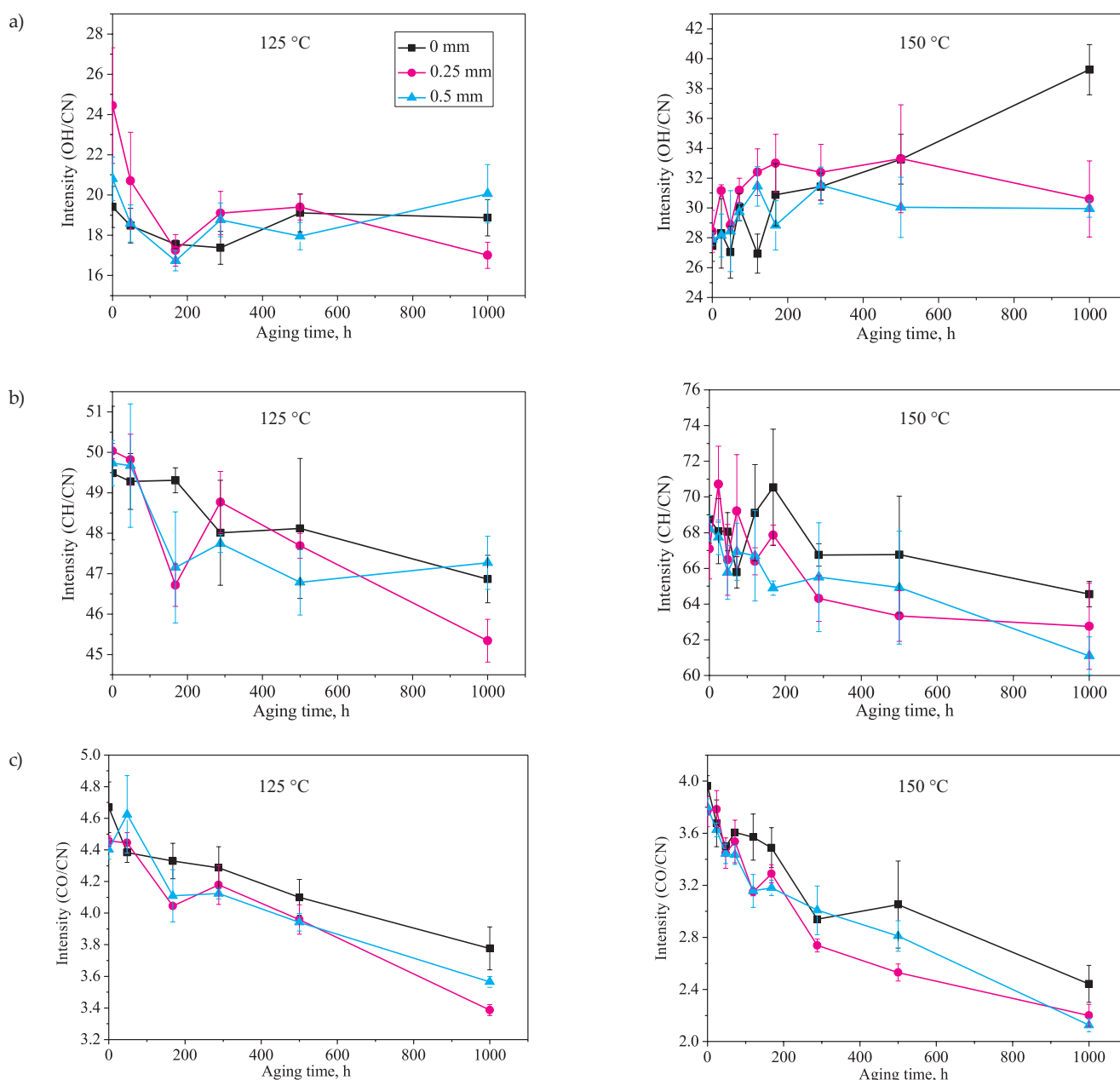


Fig. 1. Effect of temperature and aging time of HNBR on relative peak intensities (using C≡N group as reference) of groups: a) O-H, b) C-H, c) C=O

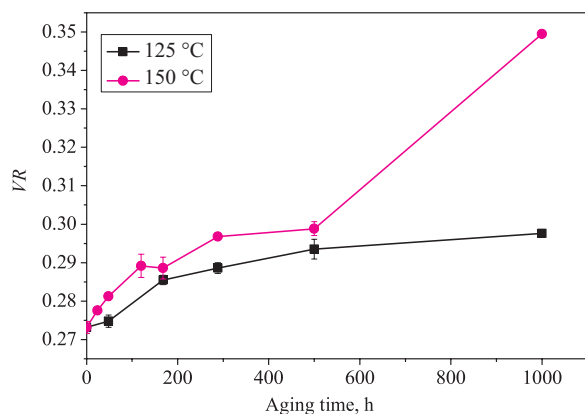


Fig. 2. Effect of aging time and temperature on crosslinking density of HNBR determined by solvent swelling test

terminated by ATR-FTIR method using the peak intensity of cyano group ( $C\equiv N$ ,  $2233\text{ cm}^{-1}$ ) as reference. Changes of relative peak intensities of O-H and C=O groups represent the changes of the content of oxidative products. Changes of relative peak intensities of C=O and C-H groups represent the changes of the content of additives. As is shown in Fig. 1a, the intensity of O-H group remained almost unchanged at  $125\text{ }^{\circ}\text{C}$ ; at  $150\text{ }^{\circ}\text{C}$  the intensity increased only on the surface after 500 h. The intensity of C-H group decreased gradually at two temperatures attributed to the loss of additives (discussed later); there was no obvious difference along the depth (Fig. 1b). The intensity of C=O group decreased, which can be attrib-

uted to the loss of additives, especially the plasticizers (Fig. 1c). No increase of C=O group was observed, indicating that no severe oxidation reaction of HNBR happened even after aging at  $150\text{ }^{\circ}\text{C}$  for 1000 h, or, the possible slight oxidation was overlapped by the loss of additives.

Change in crosslinking density was measured by solvent swelling test and the results are presented in Fig. 2. The values of VR, which represent the crosslinking density, at  $125\text{ }^{\circ}\text{C}$  increased quickly in 200 h, and then increased slowly, owing to further crosslinking of the remnant carbon-carbon double bond. At  $150\text{ }^{\circ}\text{C}$ , the VR value exhibited similar but a little greater change within 500 h, and then increased rapidly, indicating significant extra crosslinking of the rubber network and thus great increase of crosslinking density. The elasticity of the rubber decreased accordingly.

The changes of mechanical properties of HNBR aged in air at  $125$  and  $150\text{ }^{\circ}\text{C}$  are presented in Fig. 3. During thermal aging, RFB and elongation at break decreased, while tensile strength and Young's modulus increased. The changes were more rapid at  $150\text{ }^{\circ}\text{C}$  than at  $125\text{ }^{\circ}\text{C}$ . The changes of mechanical properties happened from the very beginning of the aging. This indicated that the mobility of rubber chains and thus the elasticity of the rubber decreased from the very beginning of the aging process.

### Loss of additives during thermal aging

HNBR is a complex composite composed of polymer matrix and various kinds of additives like vulcaniza-

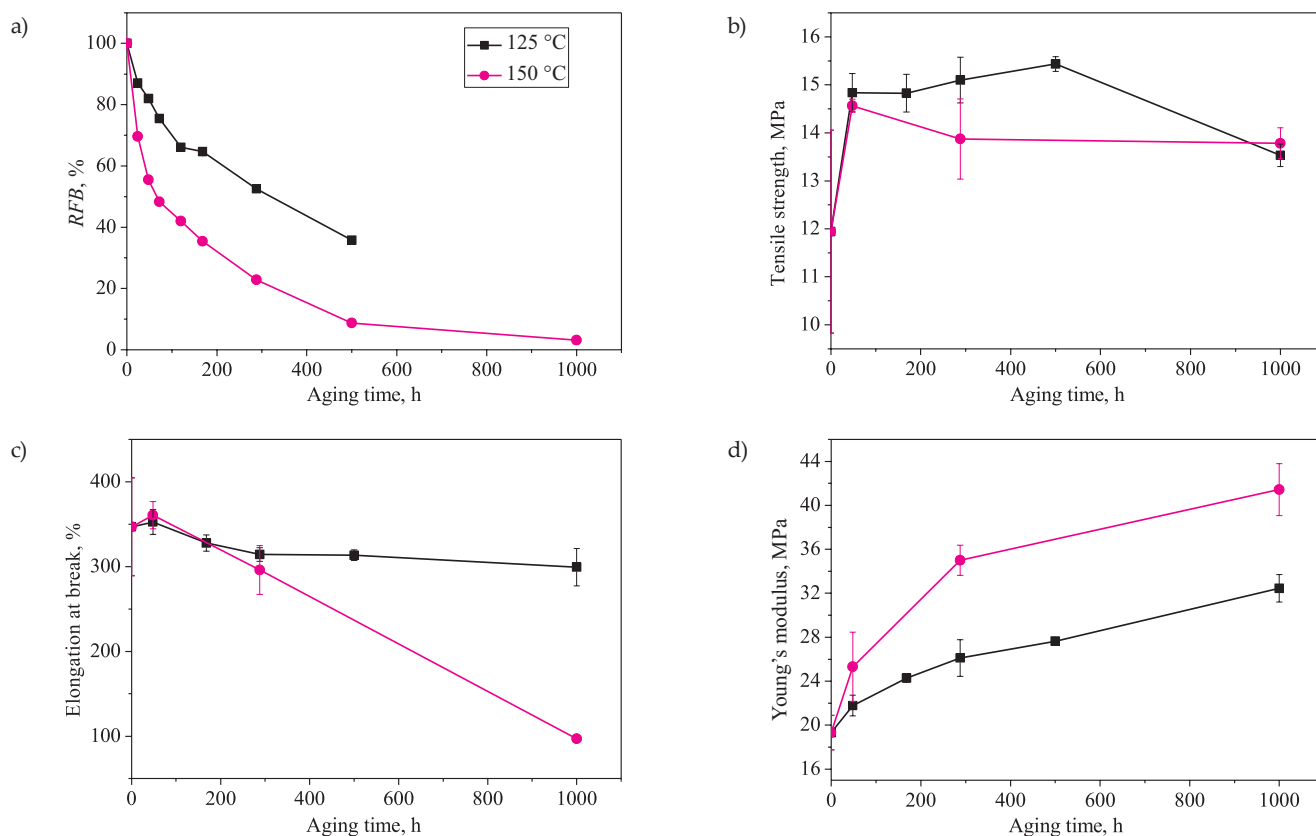


Fig. 3. Influence of aging time and temperature of HNBR on mechanical properties: a) RFB, b) tensile strength, c) elongation at break, d) Young's modulus

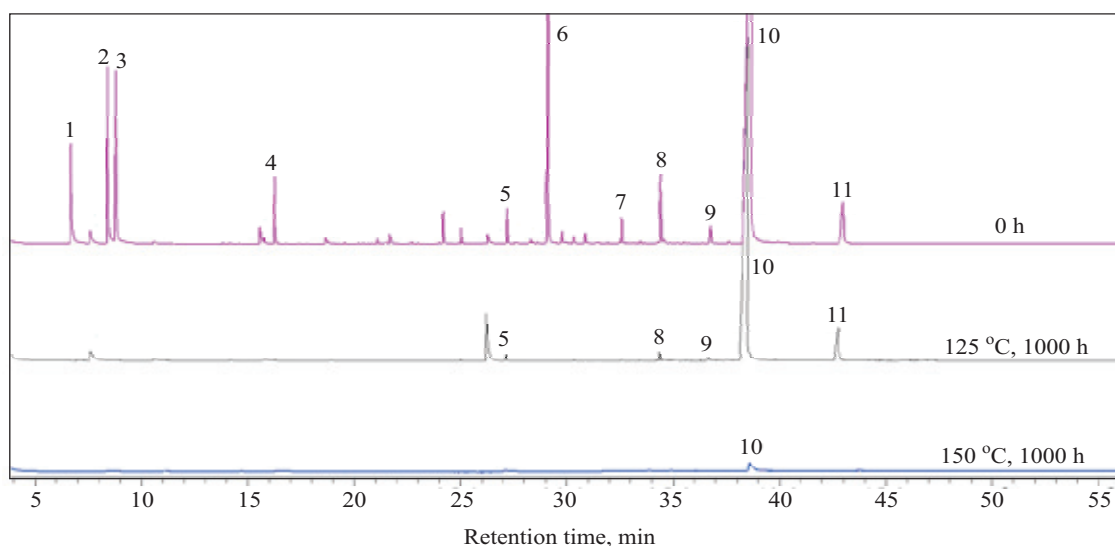


Fig. 4. Chromatograms of HNBR samples before and after aging (sampling from the surfaces of sheets)

tion agents, processing agents, plasticizers and stabilizers. Most of the additives are volatile and can be directly analyzed by flash evaporation of Py-GC/MS. Results of analysis of the samples before and after aging are shown in Fig. 4. Eleven kinds of additives were identified in the sample of HNBR, and their structures are listed in Table 1. Among them, peaks 1, 2 and 3 are attributed to the reactants of curing agents; peaks 5, 6, 7, 8, 9 and 10 are attributed to plasticizers; and peaks 4 and 11 are attributed to antioxidants. The most significant change during the thermal aging was the decrease of the peak intensities of additives. After aging at 150 °C for 1000 h, nearly all the additives in the rubber were lost.

Peak intensity changes of the reactants of curing agents, plasticizers and antioxidants during thermal aging of HNBR were plotted in Figs. 5–7. The reactants of curing agents migrated rapidly and disappeared after aging at 125 °C for only 48 h (Fig. 5). Different plasticizers had different migration rates (Fig. 6). Plasticizer DOP (peak 6) migrated rapidly and disappeared after aging at 125 °C for about 200 h. Other plasticizers including aliphatic esters and plasticizer TOTM (peak 10), migrated relatively slowly and remained in the rubber for quite a long time. The migration of plasticizers was slower at 125 °C than at 150 °C. There was no obvious difference along the depth. Similarly, different antioxidants had different migration rates (Fig. 7). Antioxidant KY-405 (peak 11) remained in the rubber longer than antioxidant 264 (peak 4). The migration of antioxidants was slower at 125 °C and there was no obvious difference along the depth. Since plasticizers and antioxidants remained in the rubber throughout most time of the aging process, it is necessary to pay great attention to their protection to the rubber network.

#### Thermal aging mechanism of HNBR

In order to describe the thermal aging process of HNBR, the time-temperature superposition principle

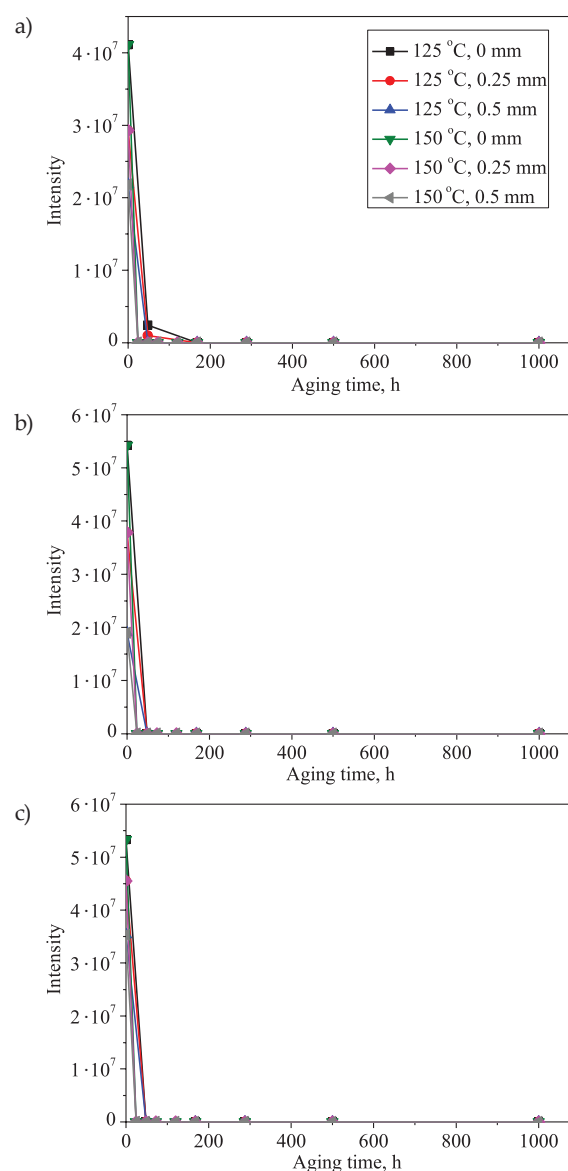


Fig. 5. Influence of aging time and temperature during thermal aging of HNBR on peak intensity changes of reactants of curing agents detected as peak: a) 1, b) 2, c) 3

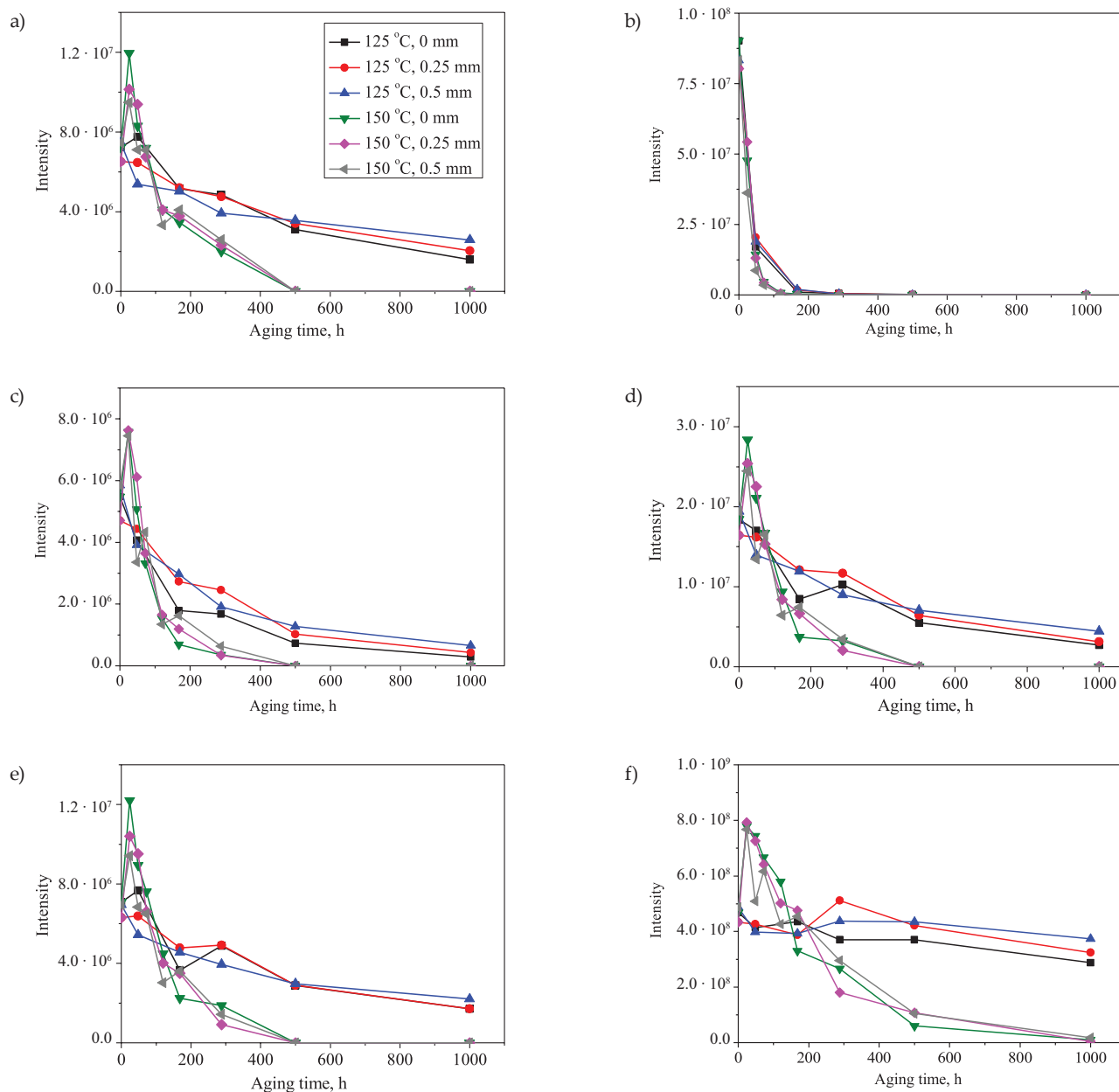


Fig. 6. Influence of aging time and temperature during thermal aging of HNBR on peak intensity changes of plasticizers detected as peak: a) 5, b) 6, c) 7, d) 8, e) 9, f) 10

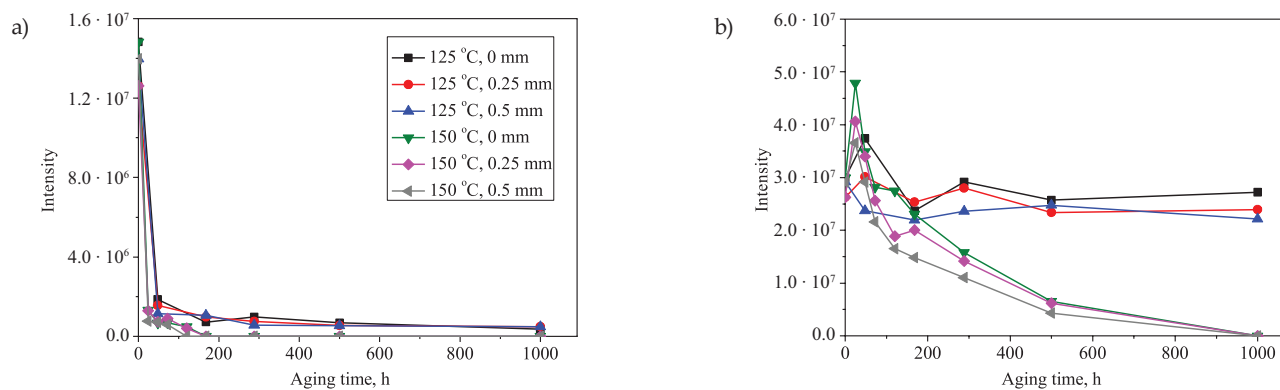
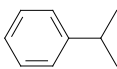
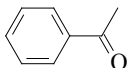
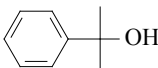
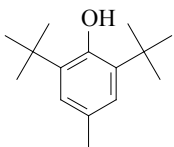
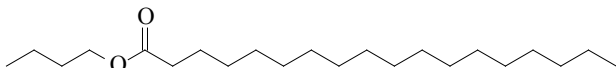
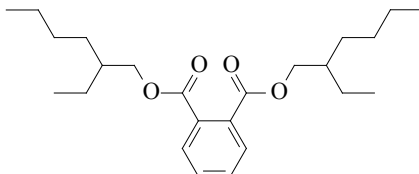
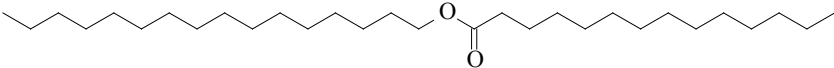
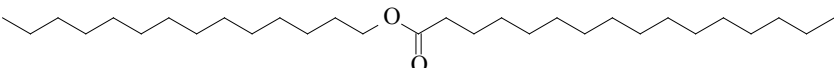
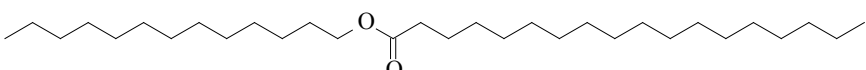
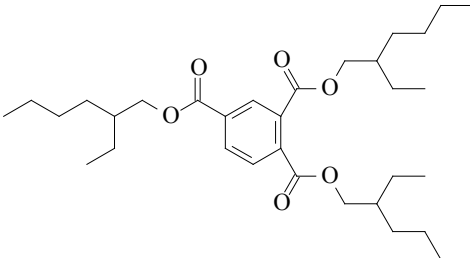
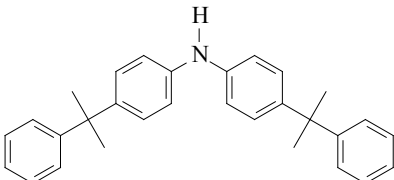


Fig. 7. Influence of aging time and temperature during thermal aging of HNBR on peak intensity changes of antioxidants detected as peak: a) 4, b) 11

Table 1. Additives detected in HNBR sample

Peak number	Retention time, min	Structure	Source
1	6.661		Curing agents
2	8.396		Curing agents
3	8.786		Curing agents
4	16.270		Antioxidant 264
5	27.191		Aliphatic ester plasticizer
6	29.110		Plasticizer DOP
7	32.580		Aliphatic ester plasticizer
8	34.426		Aliphatic ester plasticizer
9	36.751		Aliphatic ester plasticizer
10	38.668		Plasticizer TOTM
11	42.998		Antioxidant KY-405

[37] was used to obtain the master curves of typical parameters analyzed above. The reference temperature was 150 °C, and the results are shown in Fig. 8.

In HNBR, the high saturation level greatly promoted the oxidation resistance of the rubber chains. Therefore, the most significant change during the thermal aging was the loss of additives, along with the deterioration of mechanical properties, *i.e.*, the decrease of elasticity. When

the aging temperature was high enough and the aging time was long enough, obvious oxidation and crosslinking happened. From industrial experience, the failure point of rubber seals is considered as 40 % of *RFB*, corresponding to about 100 h at 150 °C. At that time, no obvious changes of functional groups or crosslinking density were observed, and the apparent changes involved the loss of additives, and correspondingly, the decrease of

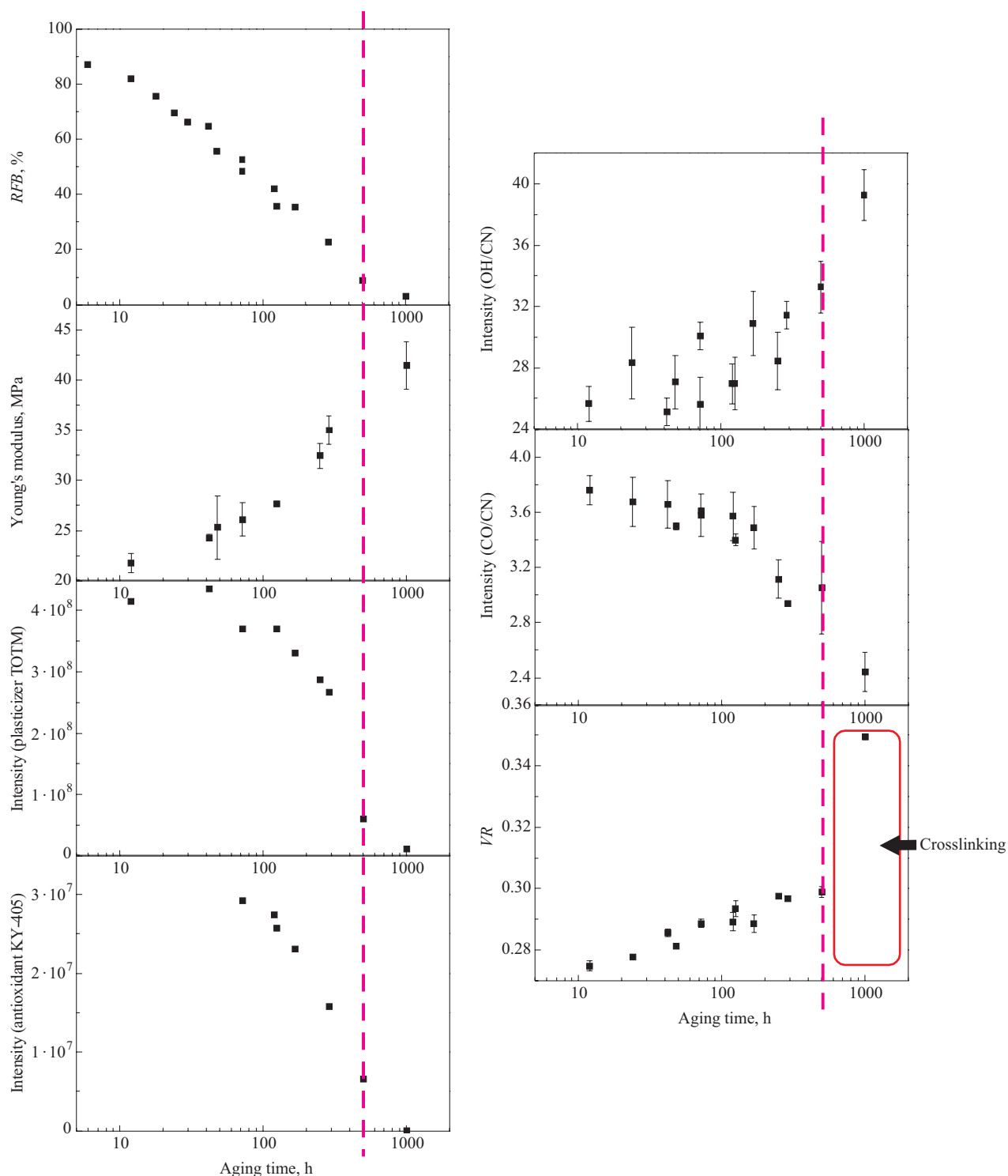


Fig. 8. Master curves of seven typical parameters of HNBR during thermal aging at 150 °C (intensities of plasticizer TOTM and antioxidant KY-405 were determined by Py-GC/MS; intensities of O-H and C=O groups were determined by ATR-FTIR, sampling from the surfaces of sheets)



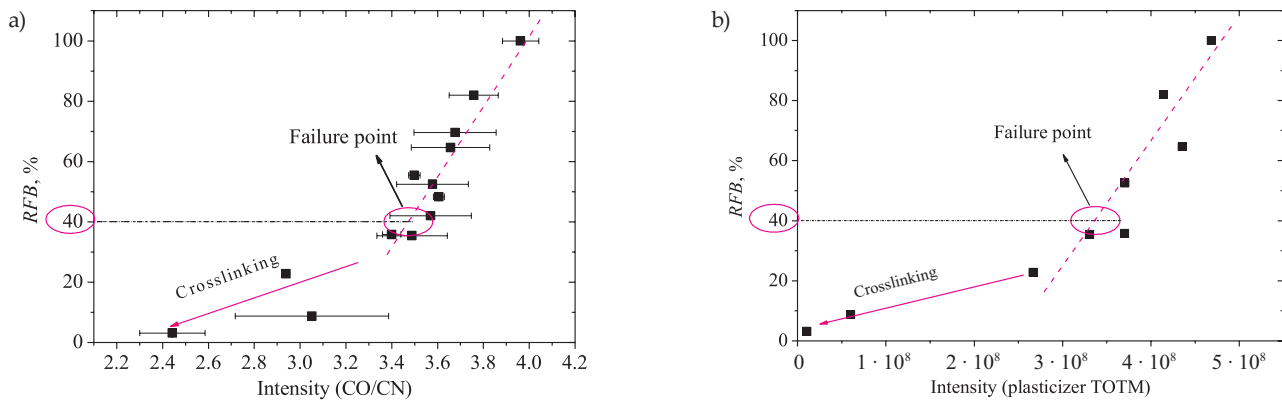


Fig. 9. Relationship between *RFB* and intensity of: a) C=O group determined by ATR-FTIR; b) plasticizer TOTM determined by Py-GC/MS (sampling from the surfaces of sheets) during thermal aging of HNBR at 150 °C

*RFB* and the increase of Young's modulus. After 500 h, obvious oxidation and extra crosslinking happened. At that time, the content of additives, both plasticizer TOTM and antioxidant KY-405, was extremely low. The rapid decrease of the content of plasticizers caused the deterioration of the mobility of rubber chains and the simultaneous rapid decrease of *RFB*. And, the residual antioxidant was not able to protect the rubber network from oxidation and crosslinking.

#### The effect of additives on elasticity maintenance

Based on the above discussion, the residual content of additives was important to the maintenance of elasticity of the rubber. Relationships between *RFB* and intensity of C=O group or plasticizer TOTM, presented in Fig. 9, were established to reveal the effect of additives.

As is shown in this figure, the failure of HNBR happened long before obvious oxidation and extra crosslinking of the rubber network. Before extra crosslinking, linear relations between *RFB* and both intensity of C=O group and plasticizer TOTM were obtained, indicating that the failure of the rubber was caused by the loss of additives, especially plasticizers, and the elasticity of HNBR

during thermal aging could be estimated by simply measuring the level of residual additives.

In order to validate the great effect of plasticizers on the maintenance of the mobility of rubber chains during thermal aging, *n*-propyl palmitate, as a representative aliphatic ester plasticizer, was used in the *RFB* recovery test of aged HNBR. Aged HNBR samples were immersed in both the *n*-propyl palmitate and IRM903 oil (a kind of commonly used lubricating oil), or just stored at ambient condition (in air). *RFB* values were measured before and after immersion and *RFB* recovery were gained. For comparison, the *RFB* recovery test of aged NBR was also carried out. NBR was much easier to be oxidized than HNBR, and severe oxidation and extra crosslinking occurred in aged NBR in this test [36]. Consequently, aged HNBR and aged NBR were in different states before immersion. When NBR was aged at 125 °C for 288 h, irreversible chemical changes happened, and the *RFB* value was 0 before immersion. When HNBR was aged at 150 °C for 72 h, the most significant change was the loss of additives, and no irreversible changes of chemical structures happened. *RFB* value of the aged HNBR was 48.3 % before immersion.

The *RFB* values of aged HNBR after immersion in three media for different times are shown in Fig. 10. Before immersion, *RFB* of 48.3 % was observed in aged HNBR without obvious oxidation or crosslinking of the

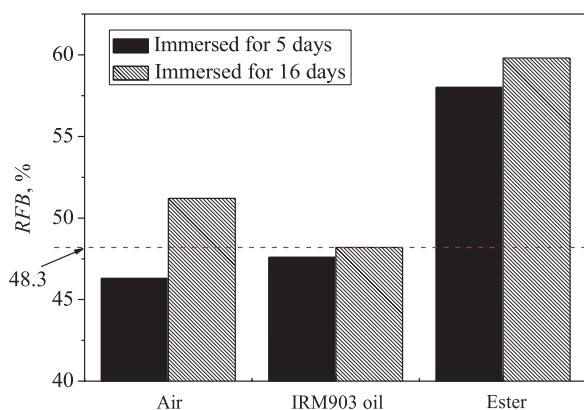


Fig. 10. *RFB* values of aged HNBR after immersion in three media for different times

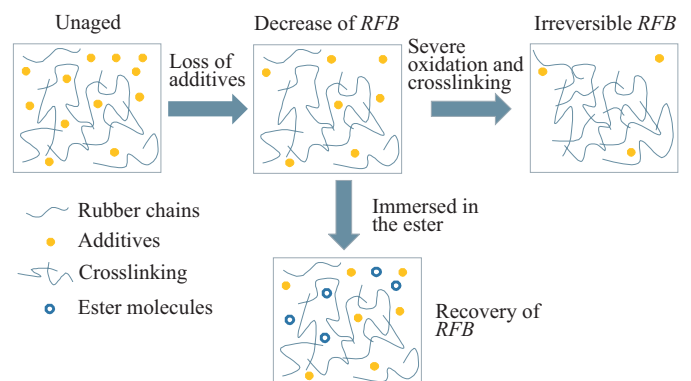


Fig. 11. Schematic diagram of the mechanism of *RFB* recovery

rubber network. After immersion in IRM903 oil for several days, the *RFB* value did not change. Storage in air for 16 days resulted in a slight increase of the *RFB* value, maybe because of relaxation. Notably, the *RFB* value of HNBR increased by 20.1–23.8 % after immersion in *n*-propyl palmitate, demonstrating that the elasticity of HNBR recovered after immersion in the ester.

On the contrary, the *RFB* recovery was not observed in NBR when it was immersed also in the same media. After aging in air at 125 °C for 288 h, severe oxidation and extra crosslinking of the rubber network happened, and no *RFB* was observed. Also, no recovery of *RFB* was observed after immersion.

The *RFB* recovery mechanism is illustrated in Fig. 11. During thermal aging, additives were lost along with the deterioration of elasticity. Before severe oxidation and crosslinking, the deterioration of elasticity was reversible by supplementing the lost additives, e.g., by immersion in the ester. The ester, as a model plasticizer, improved the mobility of the rubber chains, and thus the elasticity of the rubber recovered to some extent. However, once the chemical structures of rubber network were changed greatly by severe oxidation and crosslinking, the deterioration of elasticity was not reversible any more.

## CONCLUSIONS

Thermal aging process of HNBR was investigated. Changes of chemical structures and mechanical properties as well as loss of additives of HNBR aged in air at 125 or 150 °C were studied by several analytical methods. The aging procedure of HNBR exhibited two stages:

- loss of additives along with the deterioration of elasticity,
- obvious oxidation and extra crosslinking with further hardening and embrittlement.

The failure of HNBR happened long before obvious oxidation and crosslinking of the rubber chains. Loss of additives, especially plasticizers, was the main reason for the deterioration of elasticity.

The relationship between the deterioration of elasticity and the loss of plasticizers was established. Linear relations between *RFB* and both intensity of C=O and plasticizer TOTM were obtained, indicating that the elasticity of HNBR during thermal aging could be estimated by simply measuring the level of residual additives. The *RFB* recovery of aged HNBR immersed in the plasticizer (*n*-propyl palmitate as a model) was carried out. Before obvious oxidation and crosslinking happened, *RFB* of the rubber was repairable by immersion in the ester. However, once the chemical structures of the rubber network were changed greatly by severe oxidation and crosslinking, the deterioration of elasticity was not reversible any more. The recovery of *RFB* was a powerful proof of the great effect of plasticizers on the maintenance of elasticity of HNBR during thermal aging.

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